Fine Particulate Matter in the San Joaquin Valley: Review of Modeling Results From CRPAQS

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Mechanistic Air Quality Models

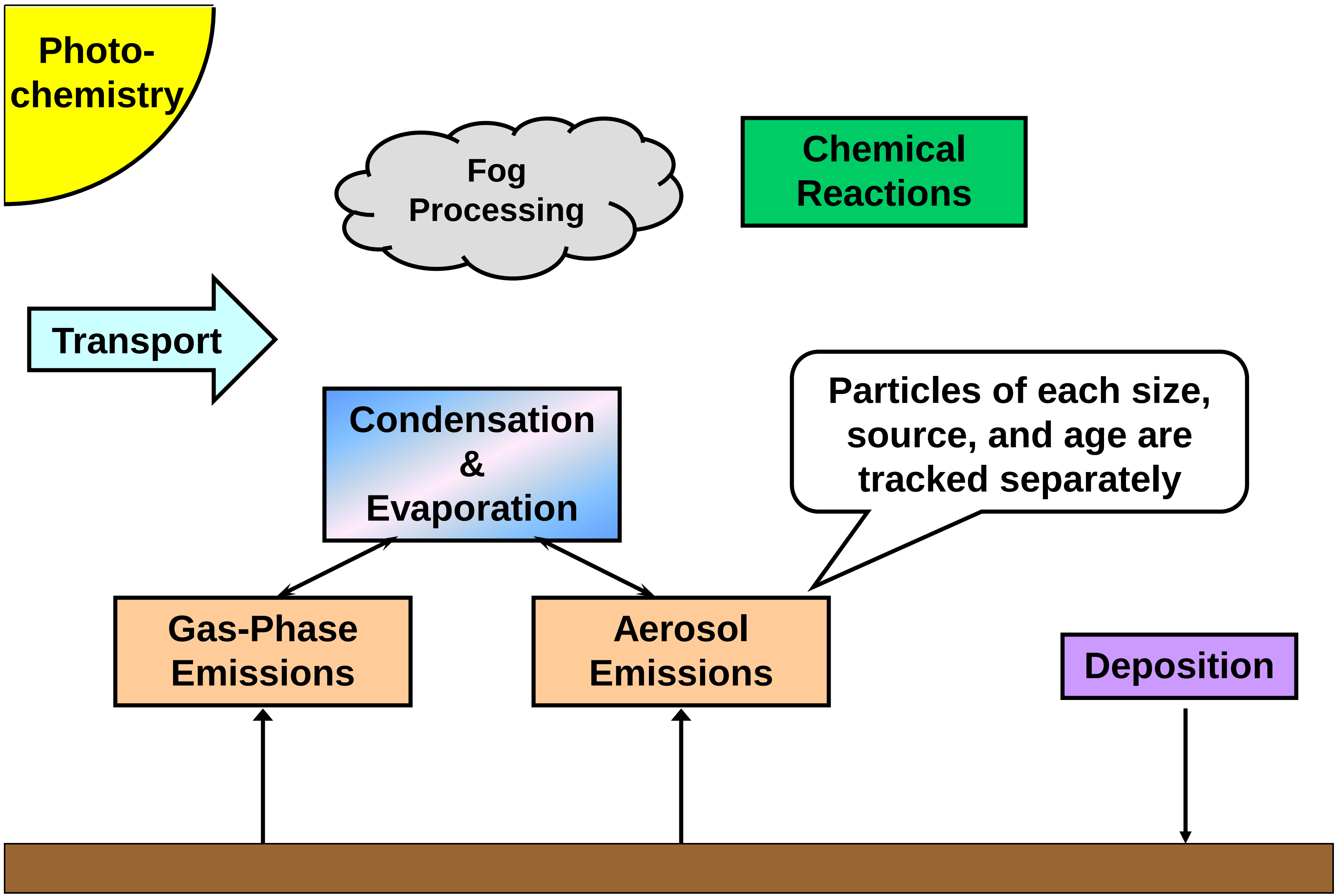


Figure courtesy of Prakash Bhave, U.S. EPA

Chemical Mechanism

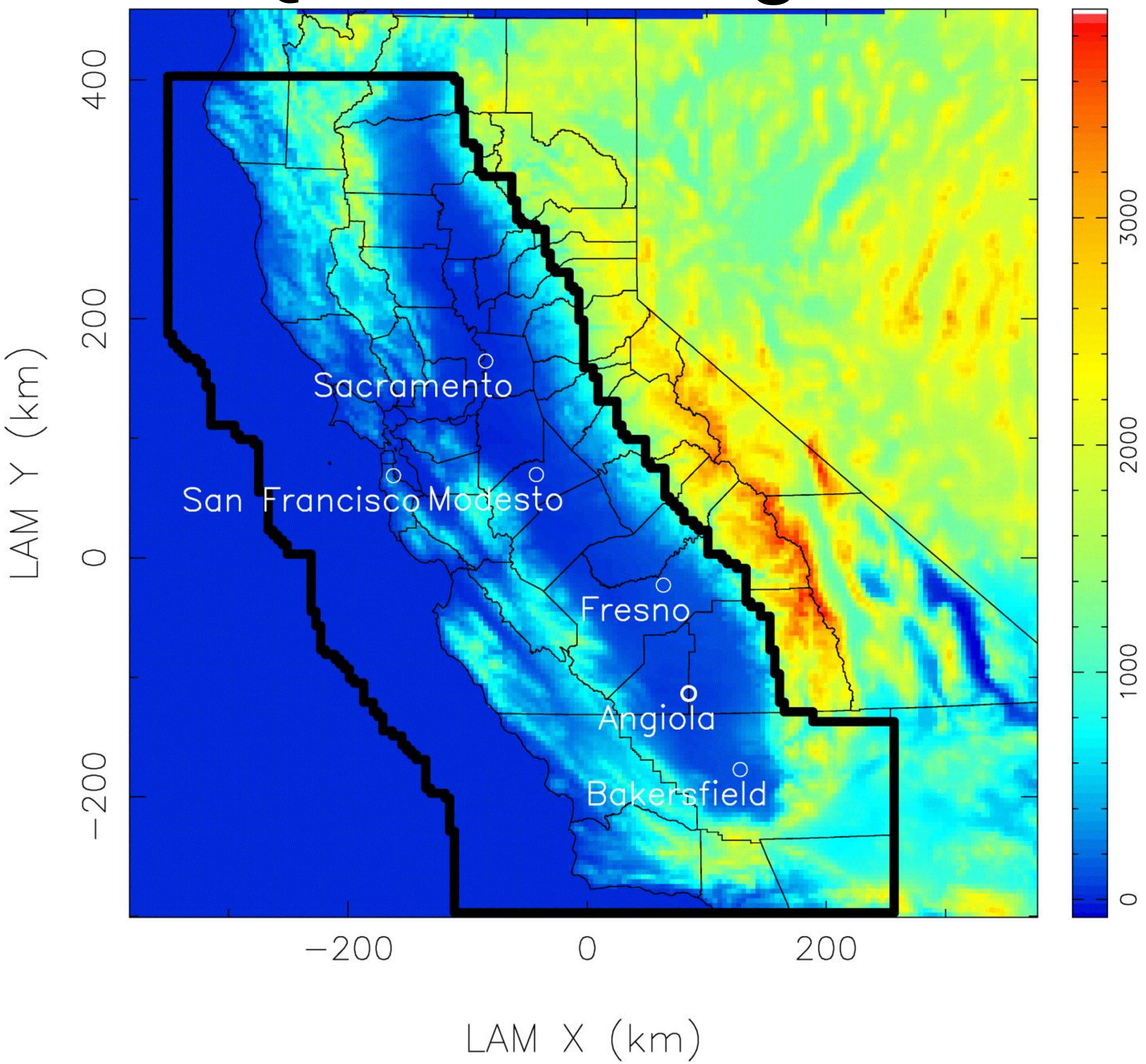
335 Active Species

15 Steady State Radicals

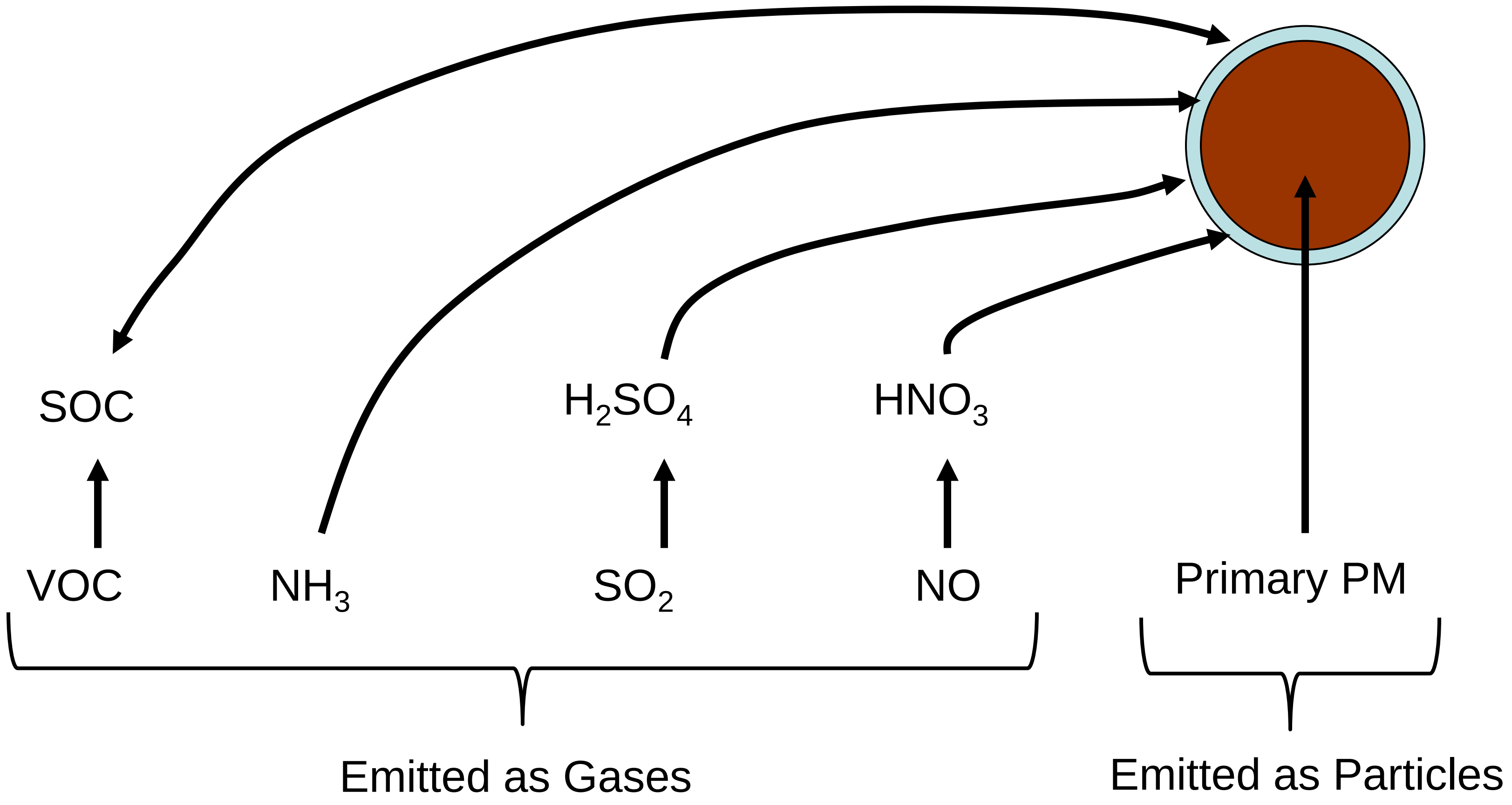
1500 Chemical Reactions

+300,000 grid cells

CRPAQS Modeling Domain



Basic Particle Chemistry



VOC = Volatile Organic Compounds (benzene, ethanol, formaldehyde, …)
SOC = semi-volatile organic compounds (mostly unknown)
Primary PM = particulate matter emitted directly from sources (trace metals – aluminum, silicon, iron, nickel, etc, elemental carbon, organic carbon)

CRPAQS PM2.5 Mass

Black Line – measurements

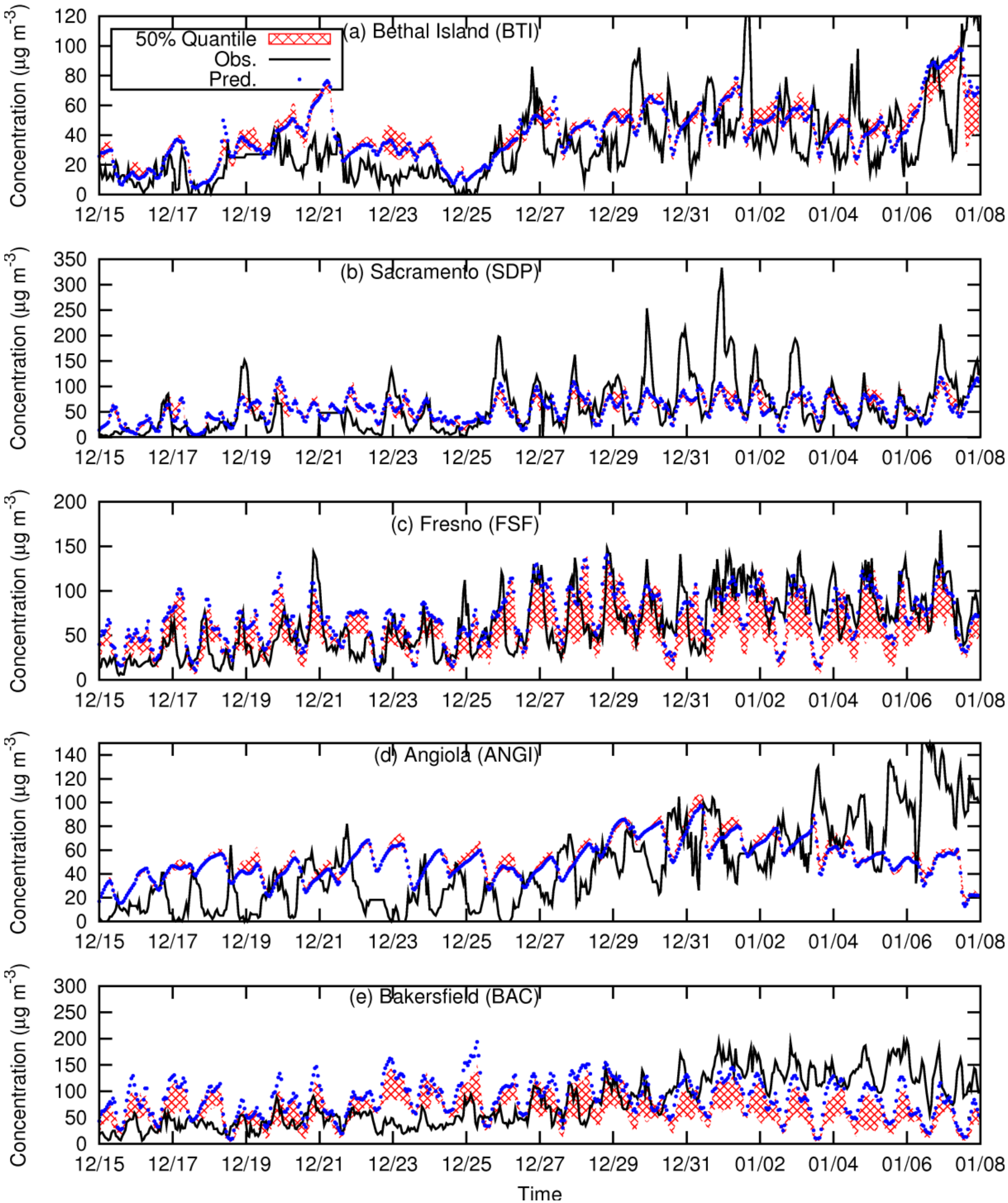
Blue Line – predictions

Red Shading – Mid 50% Quantile within 10km of monitor

Major trends are captured at most stations

Under-prediction of mass at Angiola and Bakersfield near the end of the episode

Source: Q. Ying, J. Lu, P. Allen, P. Livingstone, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part I. Base Case Model Results.", Atmos. Env., 42, pg8954-8966, 2008.

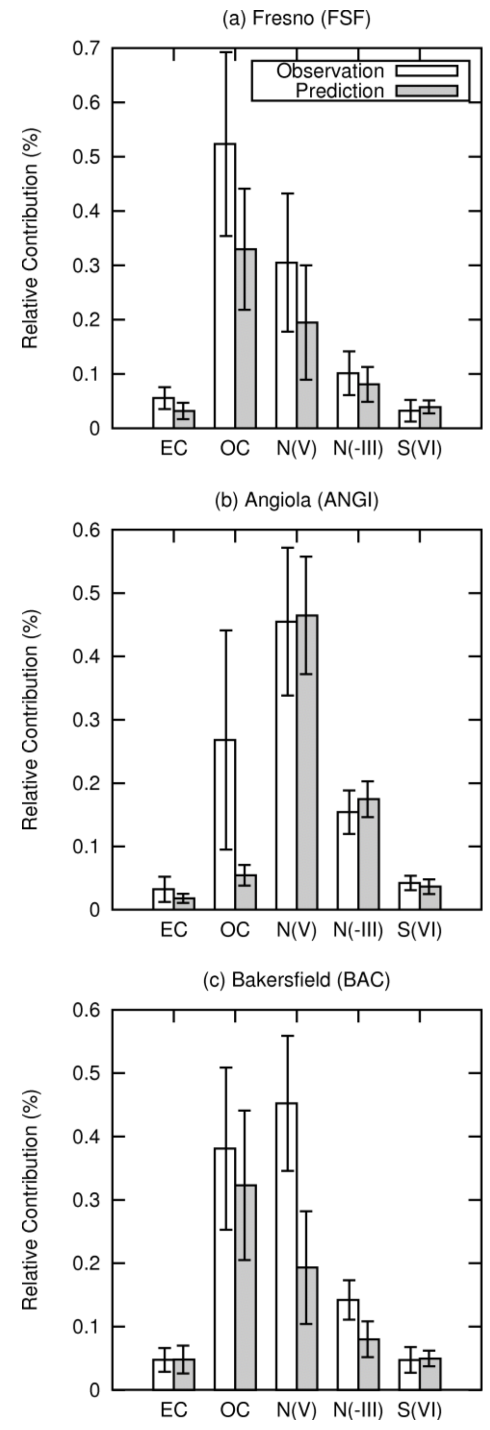


Relative Component Contributions to PM

Average and standard deviation of predictions and observations is based on 55 samples

Urban locations (Fresno and Bakersfield)
Predictions and observations match except for nitrate under-prediction at Bakersfield

Rural location (Angiola)
OC under-prediction. What primary sources are we missing? What SOA formation mechanisms are we missing?



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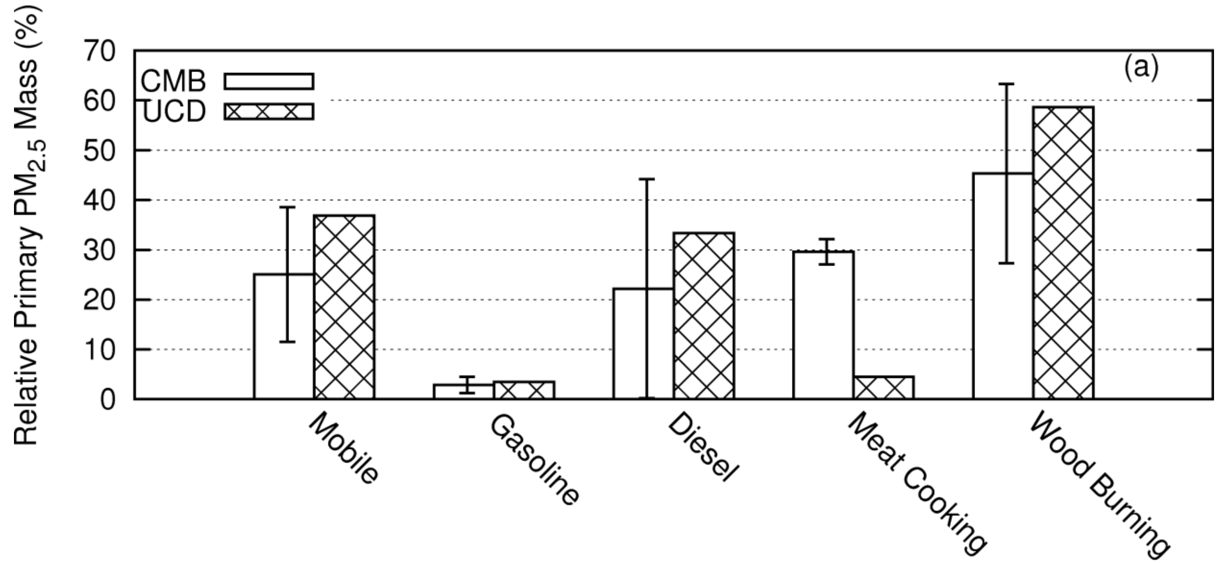
Grid Model vs. CMB Source Apportionment

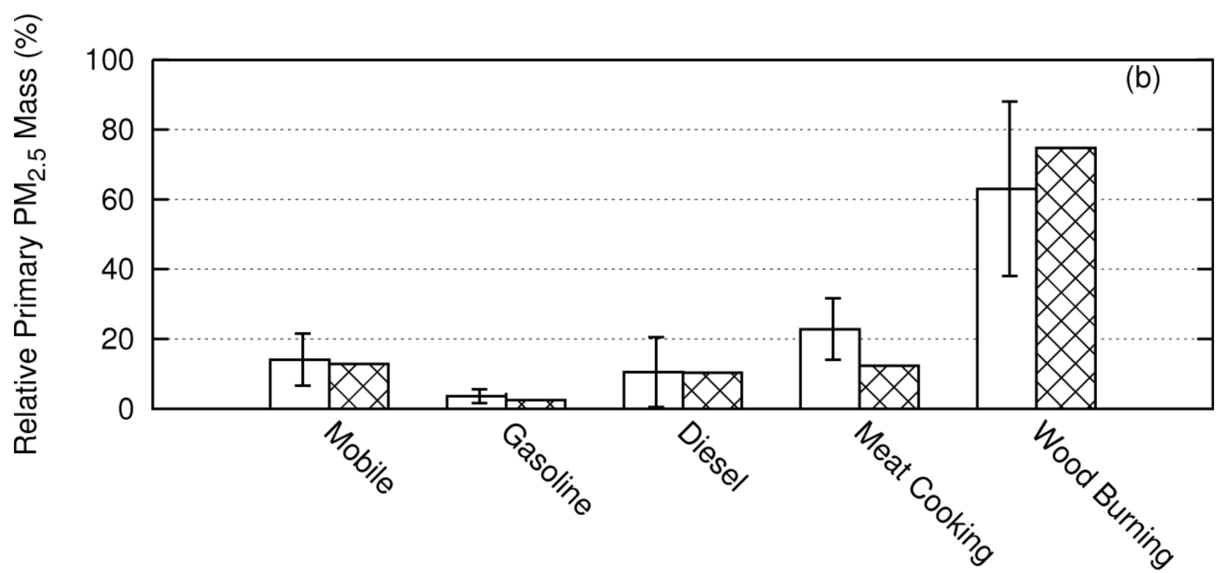
Angiola

**Dust sources removed from grid model



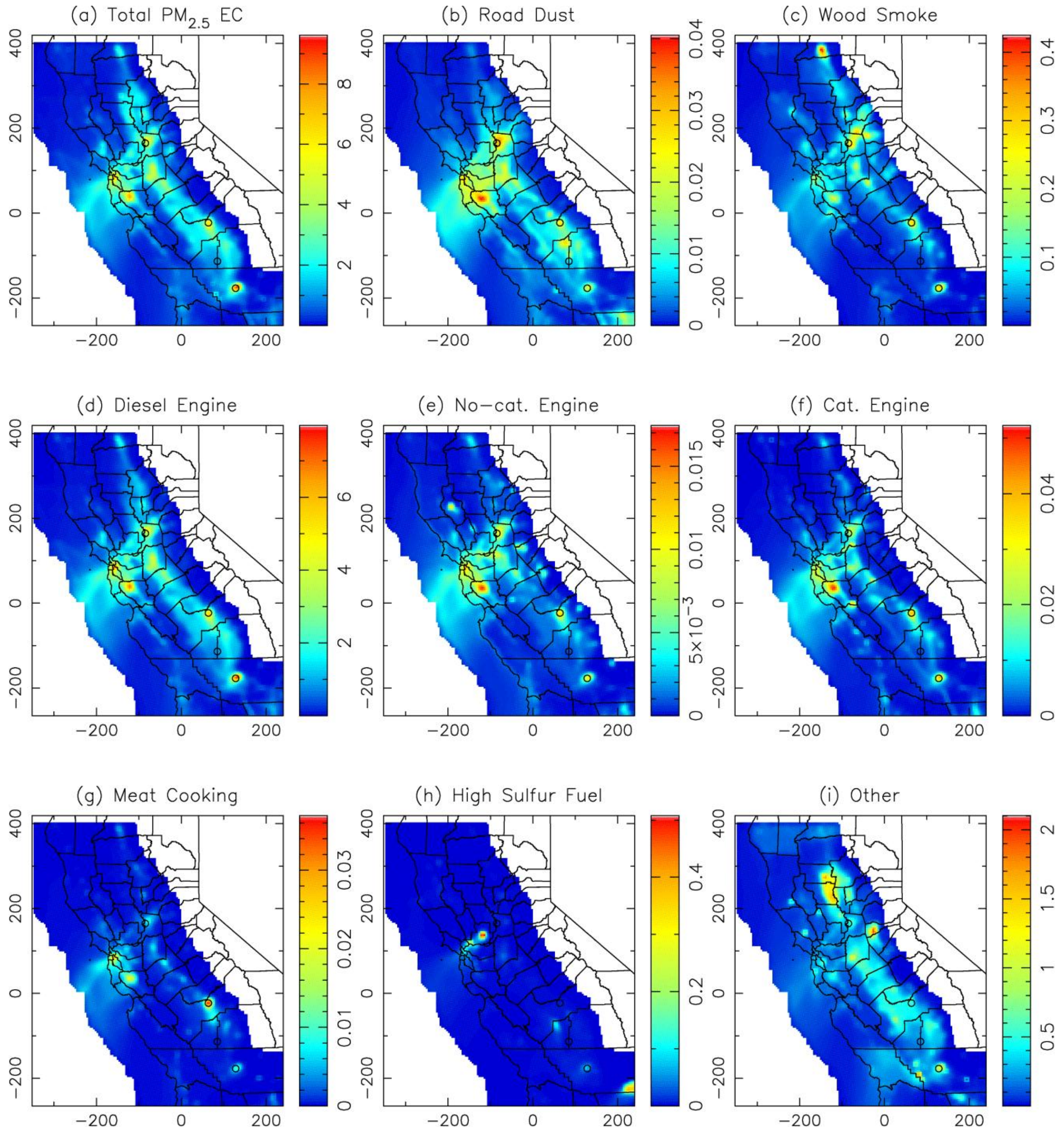
Fresno

**Dust sources removed from grid model



Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.", Atmos. Env 42, pp8967-8978, 2008.

Regional EC Source Contributions



Urban hotspots

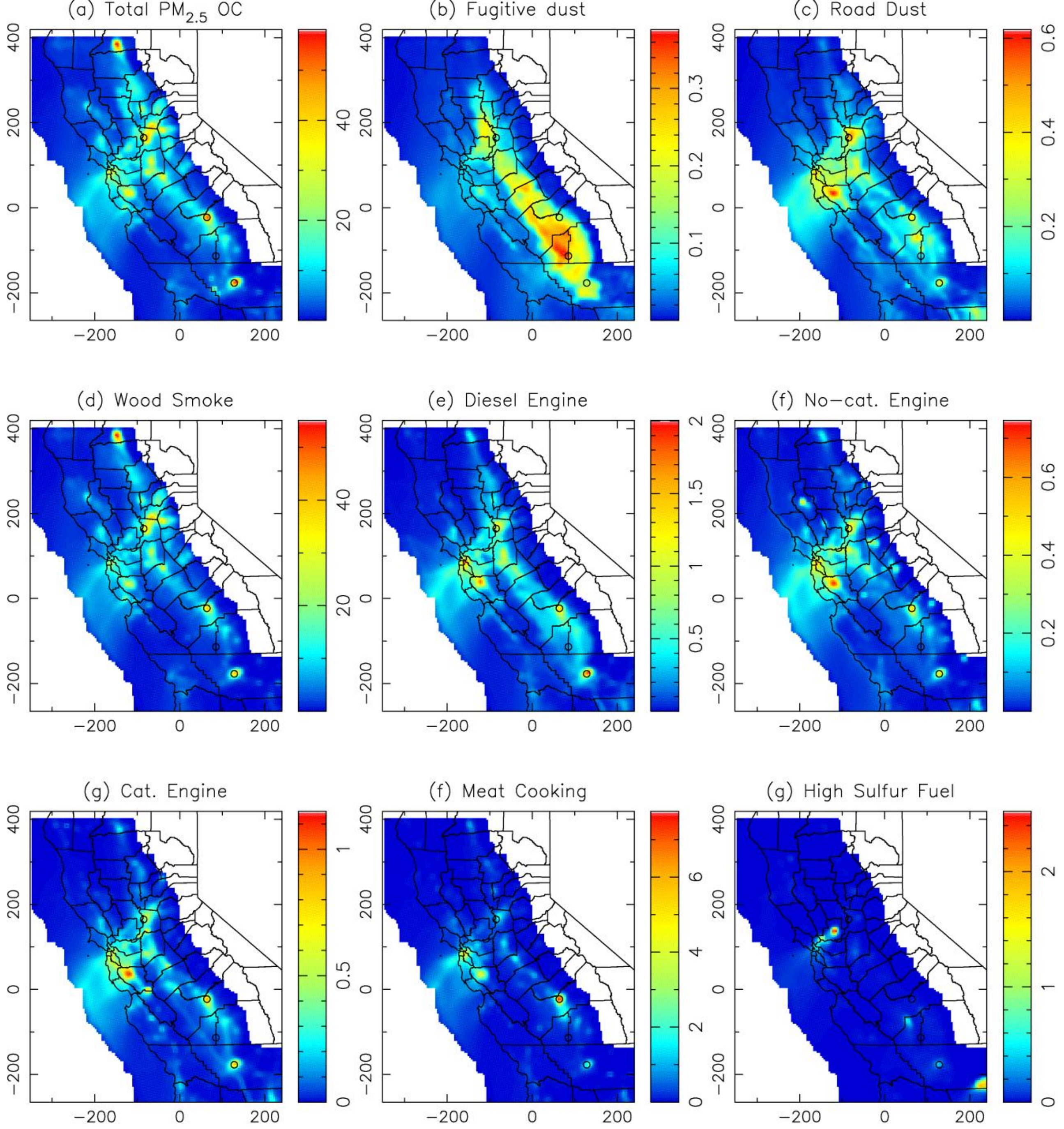
Diesel dominates

Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman "Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part II. Regional Source Apportionment of Primary Airborne Particulate Matter.", Atmos. Env., 42, pp8967-8978, 2008.

Regional OC Source Contributions

Urban hotspots

Wood smoke dominates



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Spectrum of Reactive Nitrogen Compounds

- NO, NO2, NO3, N2O5, HONO, PAN, HNO3

Reactive Intermediate Products

Direct Emissions

Stable End Product From Atmospheric Chemistry

- $HNO_3 + NH_3 \rightarrow NH_4NO_3$

Direct Emissions

Particle Phase Nitrate

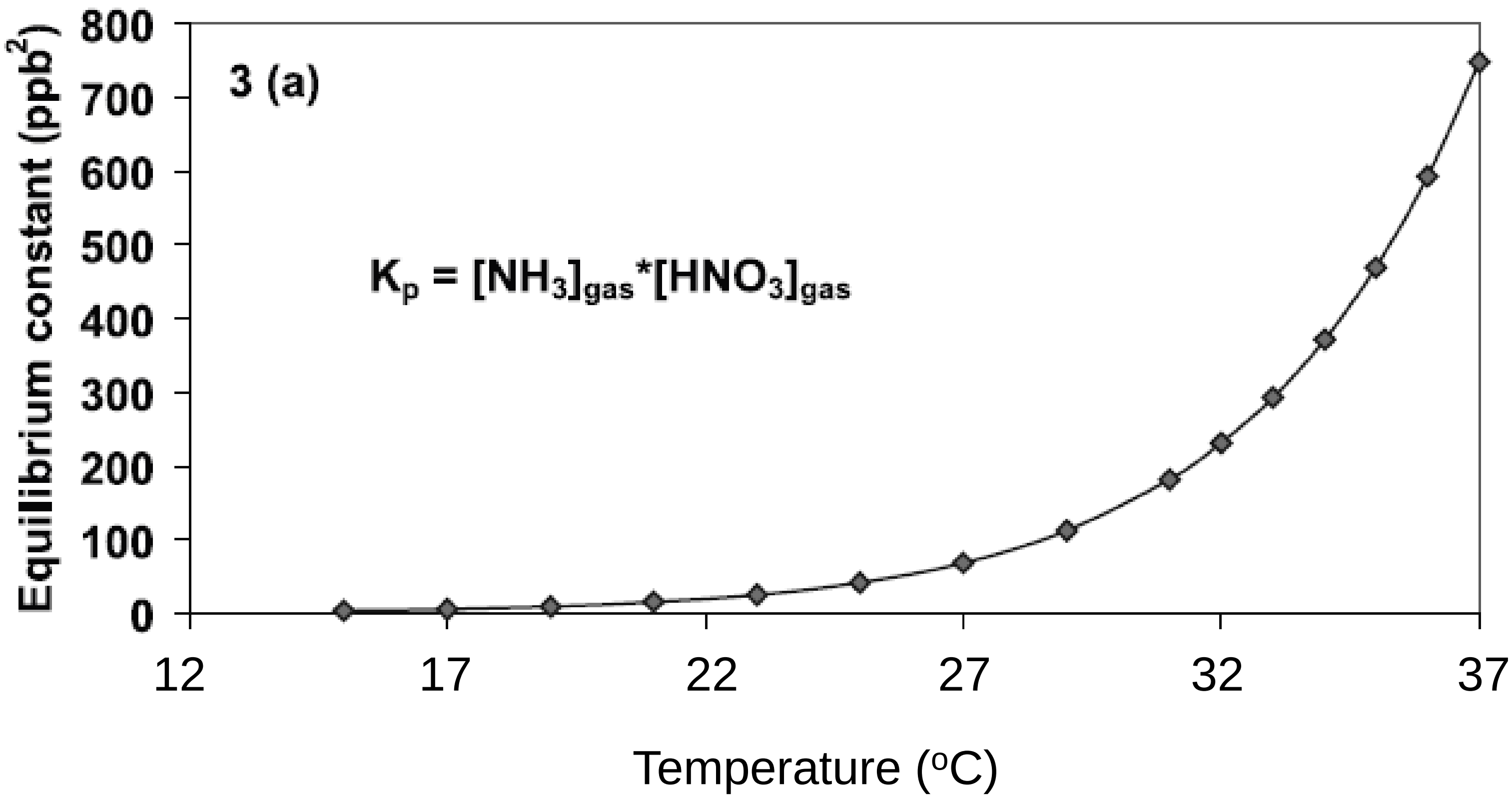
Nighttime/Winter Nitrate Formation

- $NO \xrightarrow{O_3} NO_2 \xrightarrow{O_3} NO_3 \longrightarrow N_2O_5 \xrightarrow{H_2O} 2HNO_3$

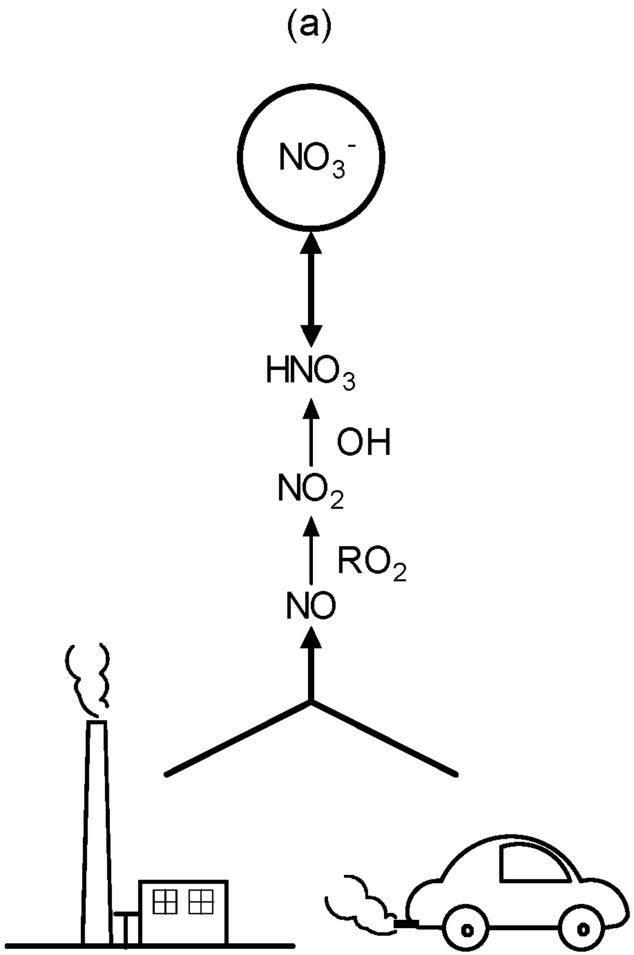
- Main oxidant is O_3 – favors low sunlight intensity, wet conditions

Equilibrium Dissociation Constant for Ammonium Nitrate

Ammonium nitrate will not form when $[NH_3]*[HNO_3] < Kp$

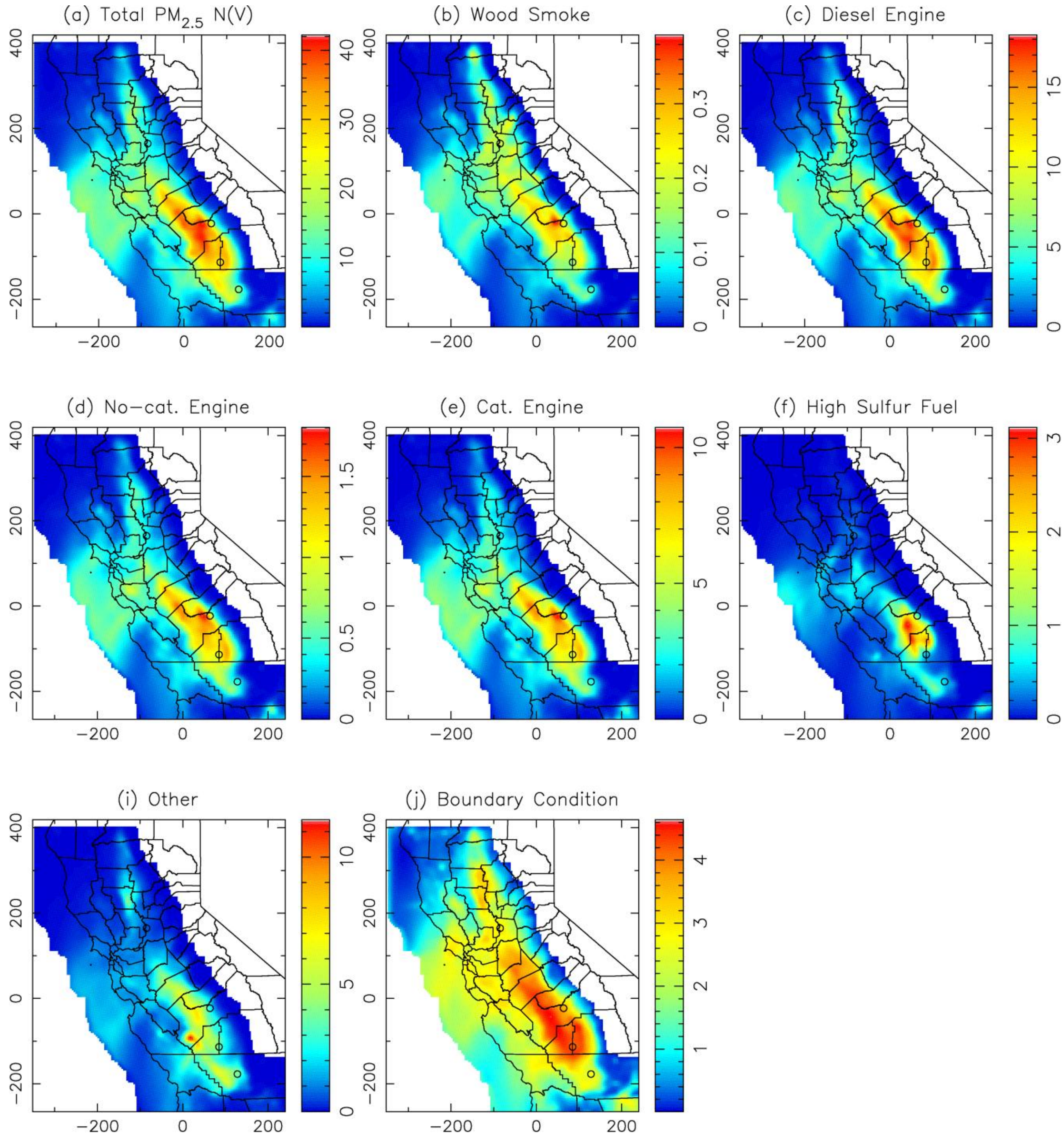


Source Apportionment of Secondary PM

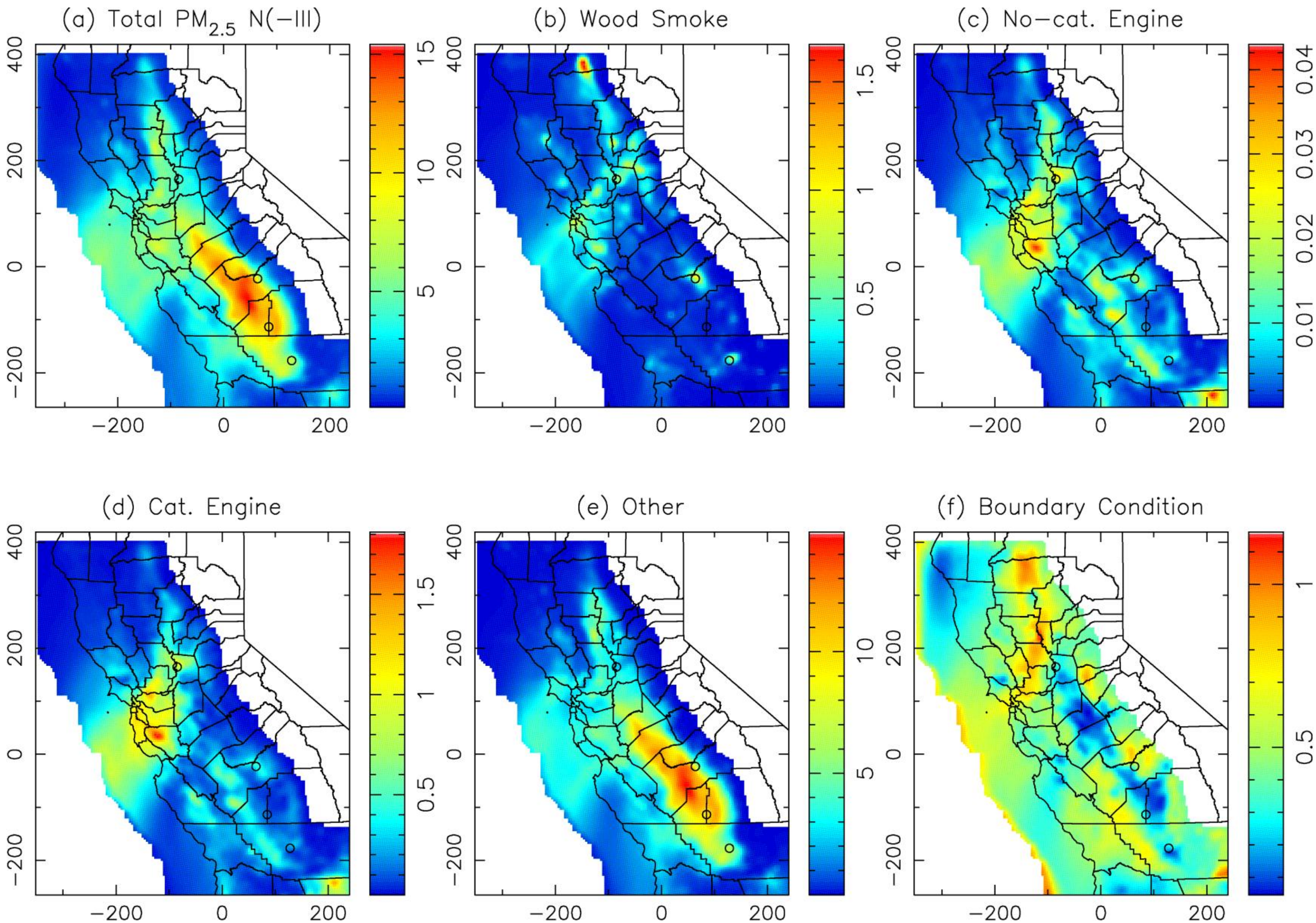


Source: Ying, Q. and M.J. Kleeman. "Source contributions to the regional distribution of secondary particulate matter in California." Atmospheric Environment, Vol 40, pp 736-752, 2006.

Regional Nitrate Source Contributions

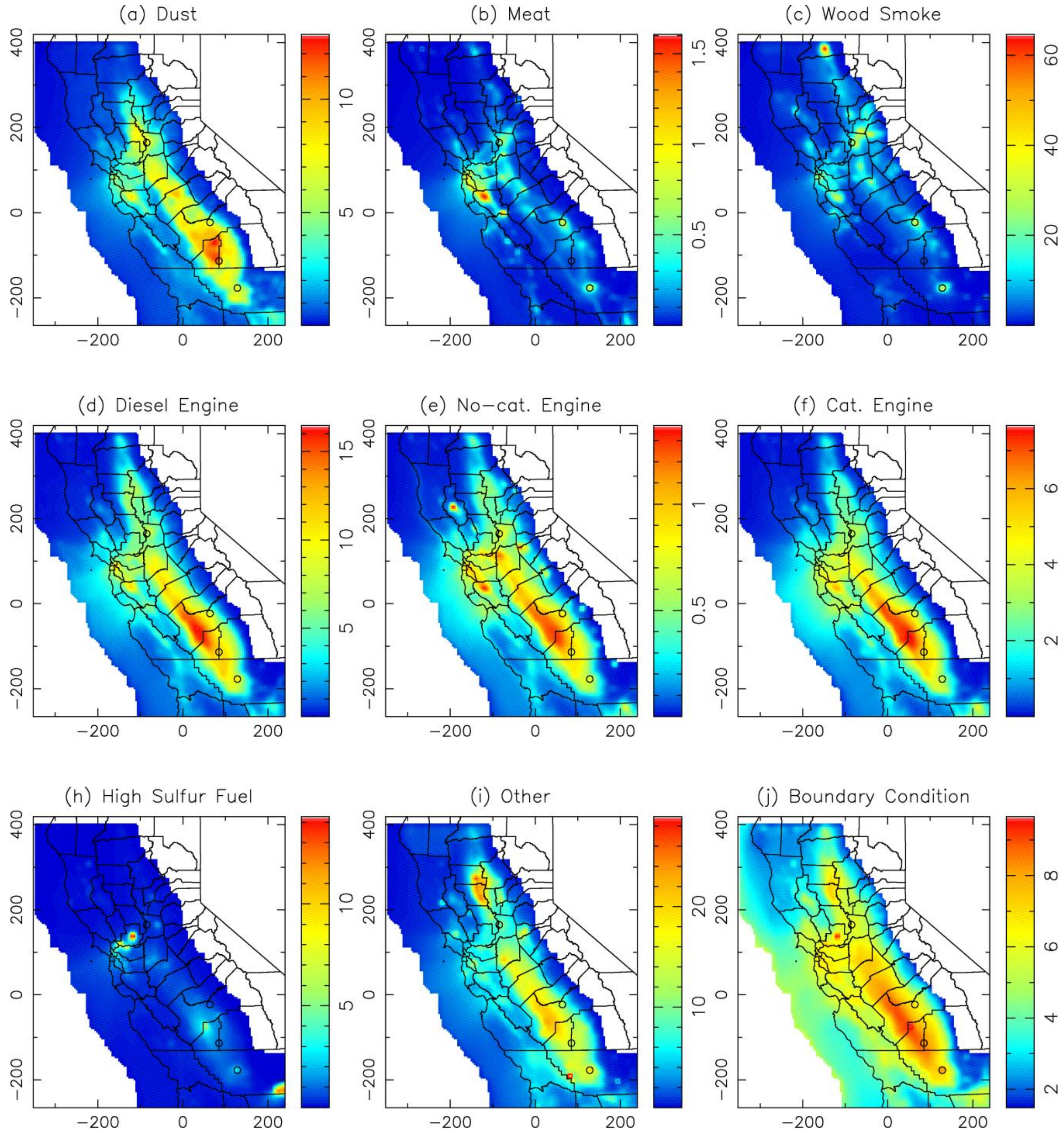


Regional NH4+ Source Contributions



Source: Q. Ying, J. Lu, A. Kaduwela, and M. Kleeman “Modeling Air Quality During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III. Regional Source Apportionment of Secondary and Total Airborne PM2.5 and PM0.1.”, Atmos. Env., 42, pp8967-8978, 2008.

Regional PM2.5 (primary + secondary) Source Contributions



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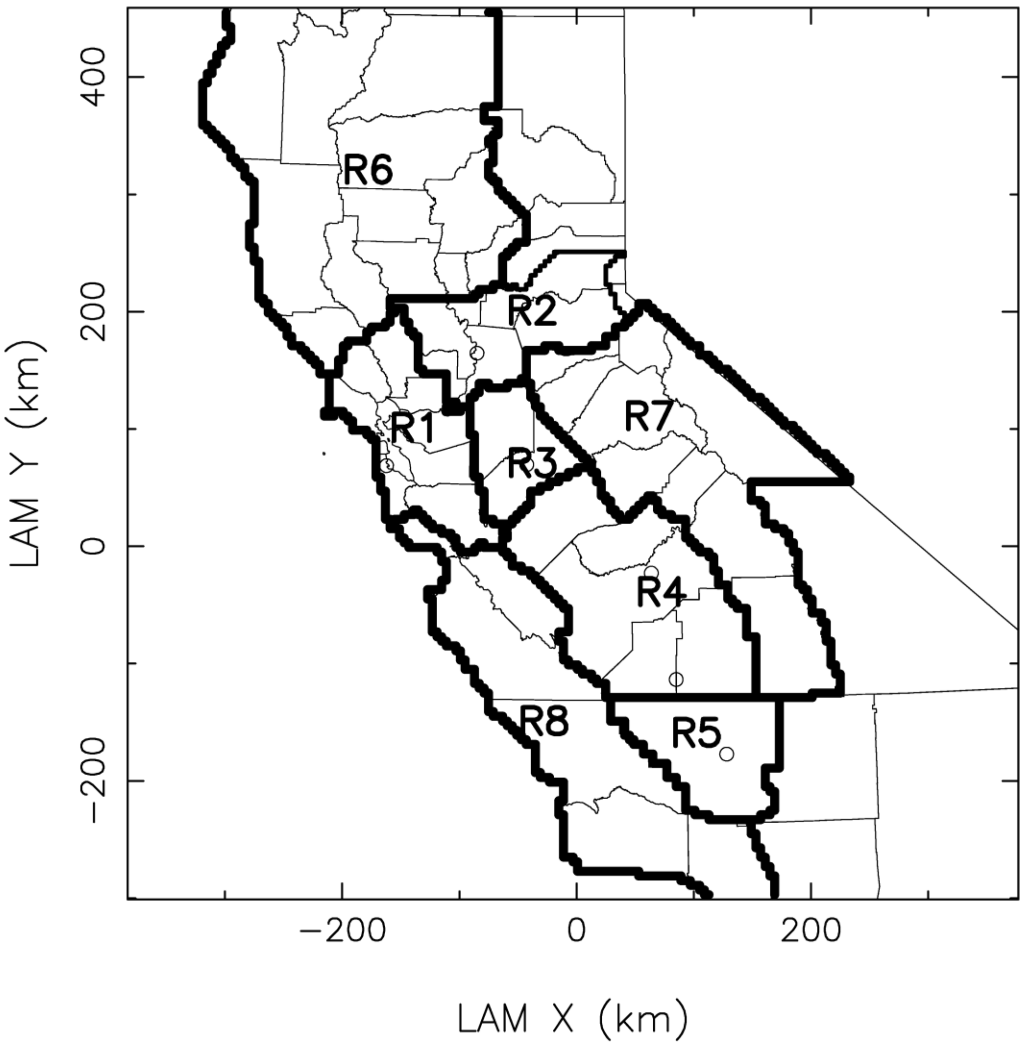
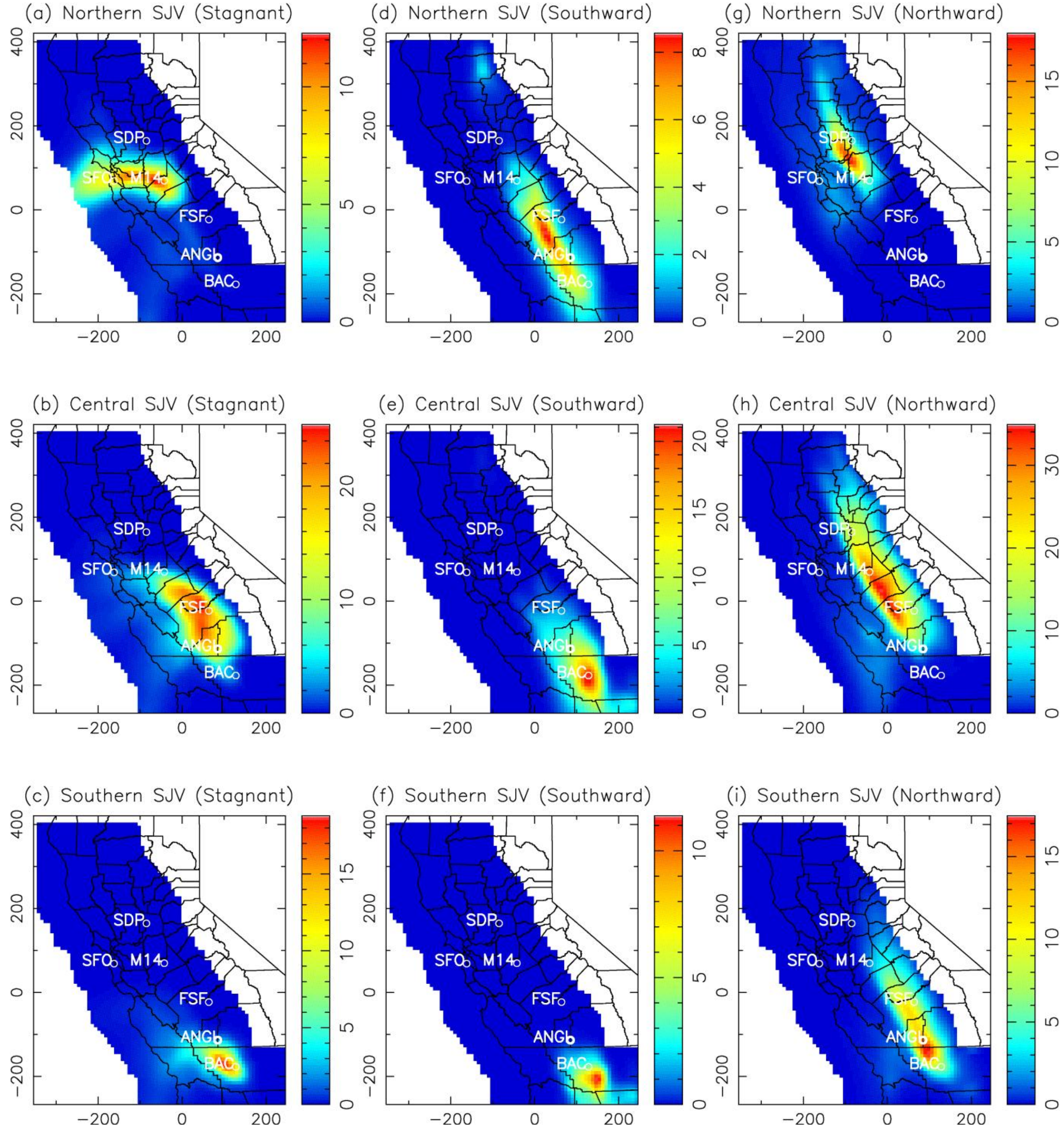
How Much PM Does Each Region Contribute to Other Regions?



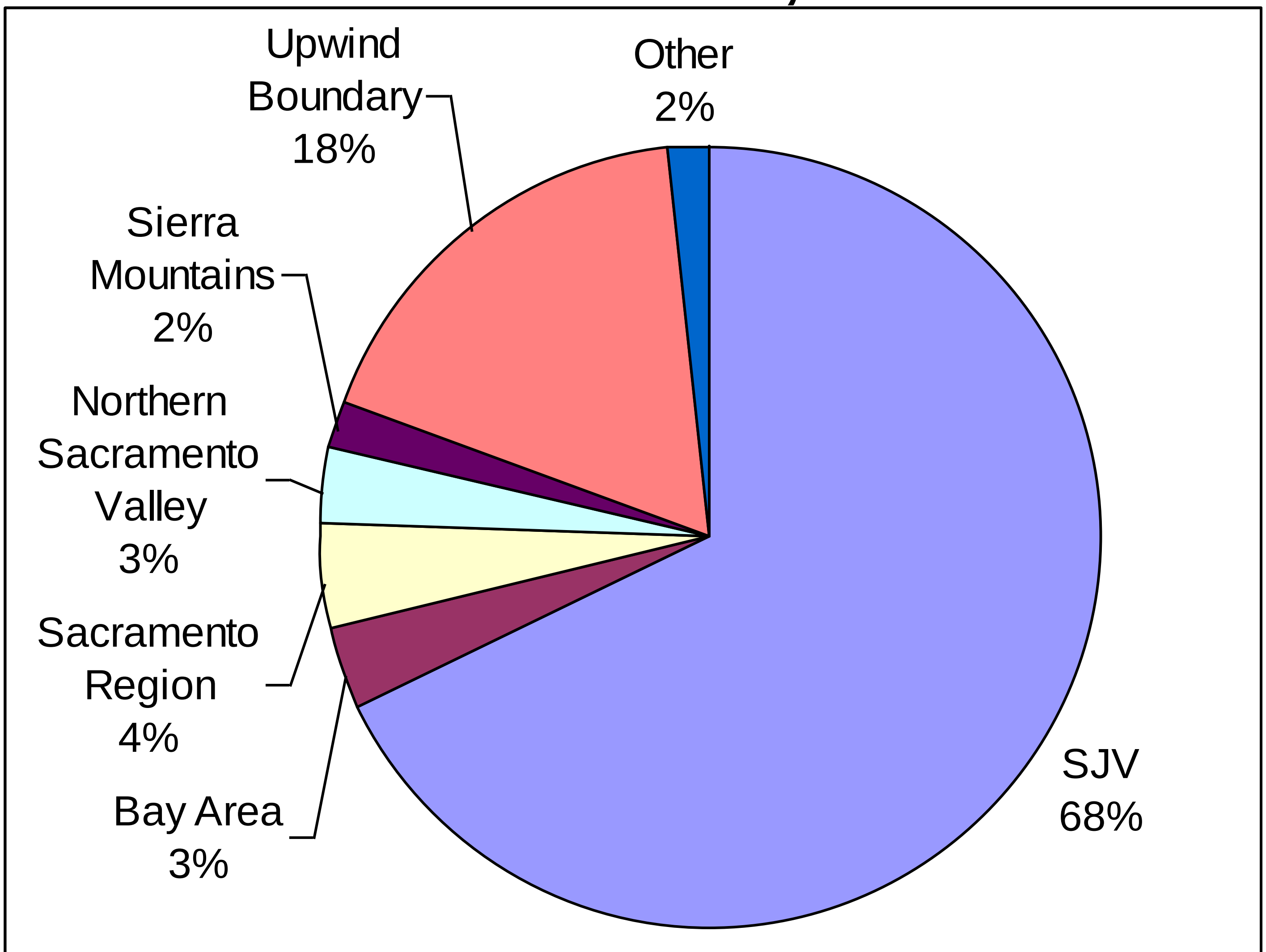
Source: Q. Ying, and M. Kleeman "Regional Contributions to Airborne Particulate Matter in Central California During a Severe Pollution Episode", Atmos. Env., 43, 1218-1228, 2009.

PM2.5 Nitrate

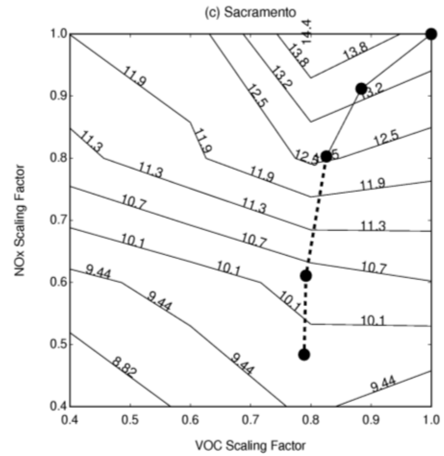


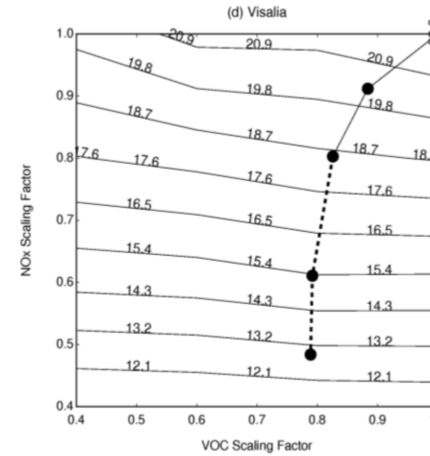
Source: Q. Ying, and M. Kleeman "Regional Contributions to Airborne Particulate Matter in Central California During a Severe Pollution Episode", Atmos. Env., 43, 1218-1228, 2009.

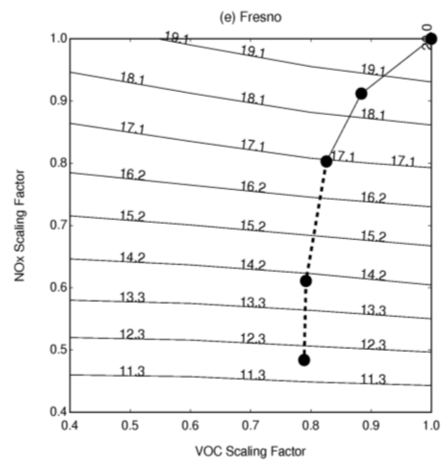
Regional Contributions to SJV PM2.5 Nitrate Between Dec 15, 2000 – Jan 7, 2001

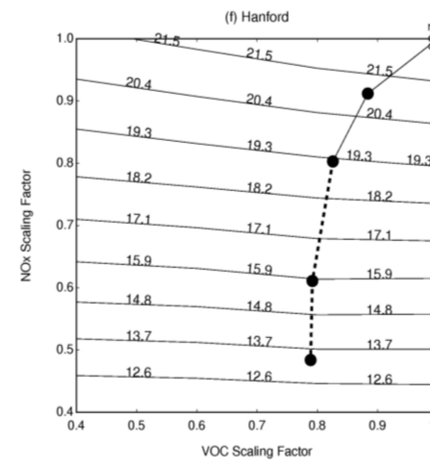


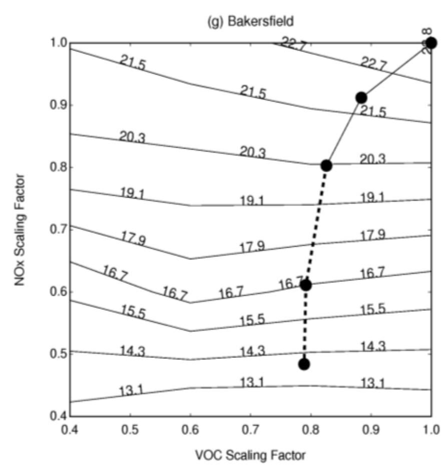
Nitrate Control Options





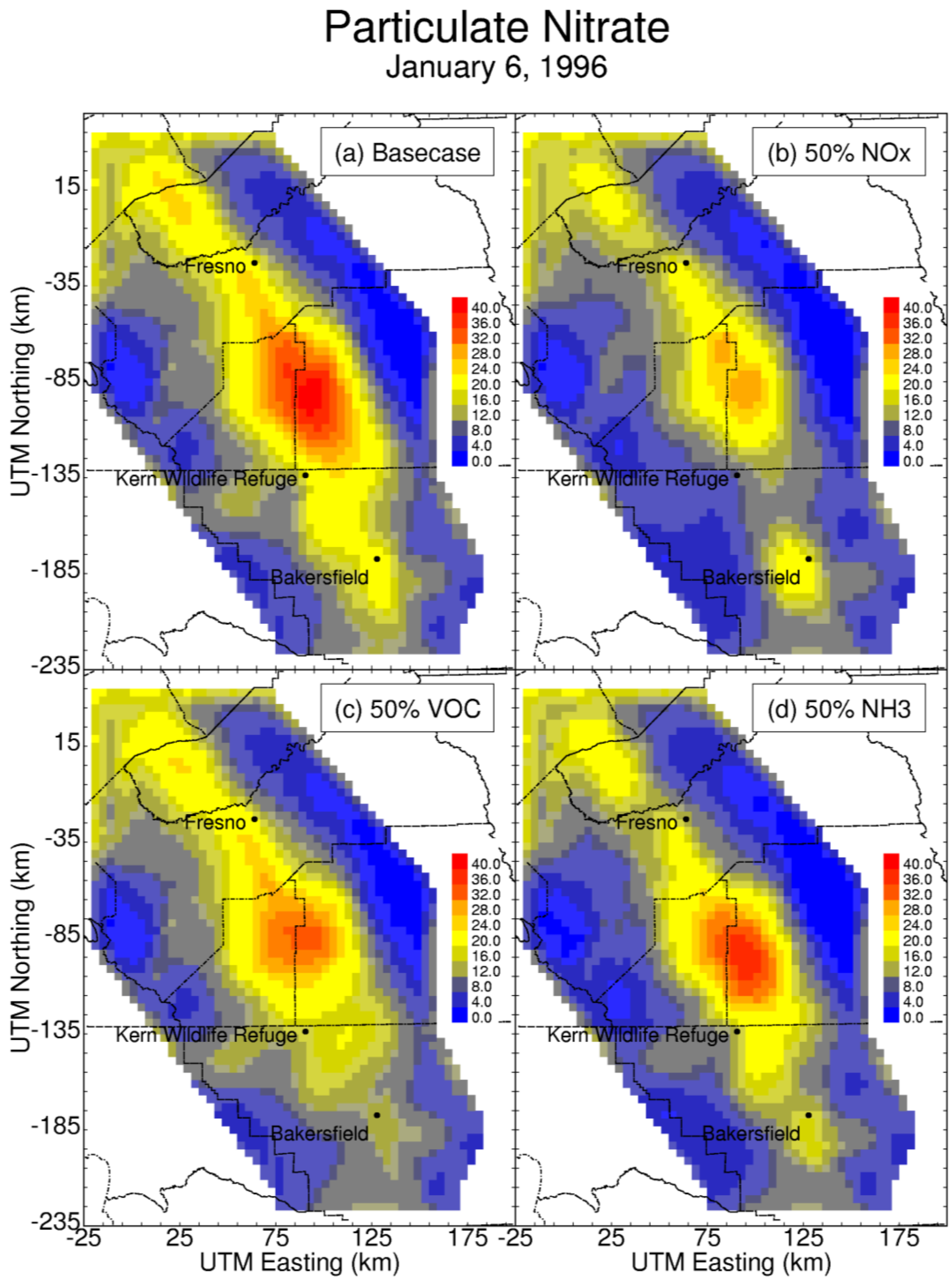






Maximum 24-hr average PM2.5 nitrate concentrations response to NOx and VOC controls on December 31, 2000 using the SAPRC 90 chemical mechanism. Solid line with dots represents estimated emissions control trajectory since the year 2000 and dashed line with dots represents projected emissions controls through the year 2020 based on the California Almanac for Emissions.

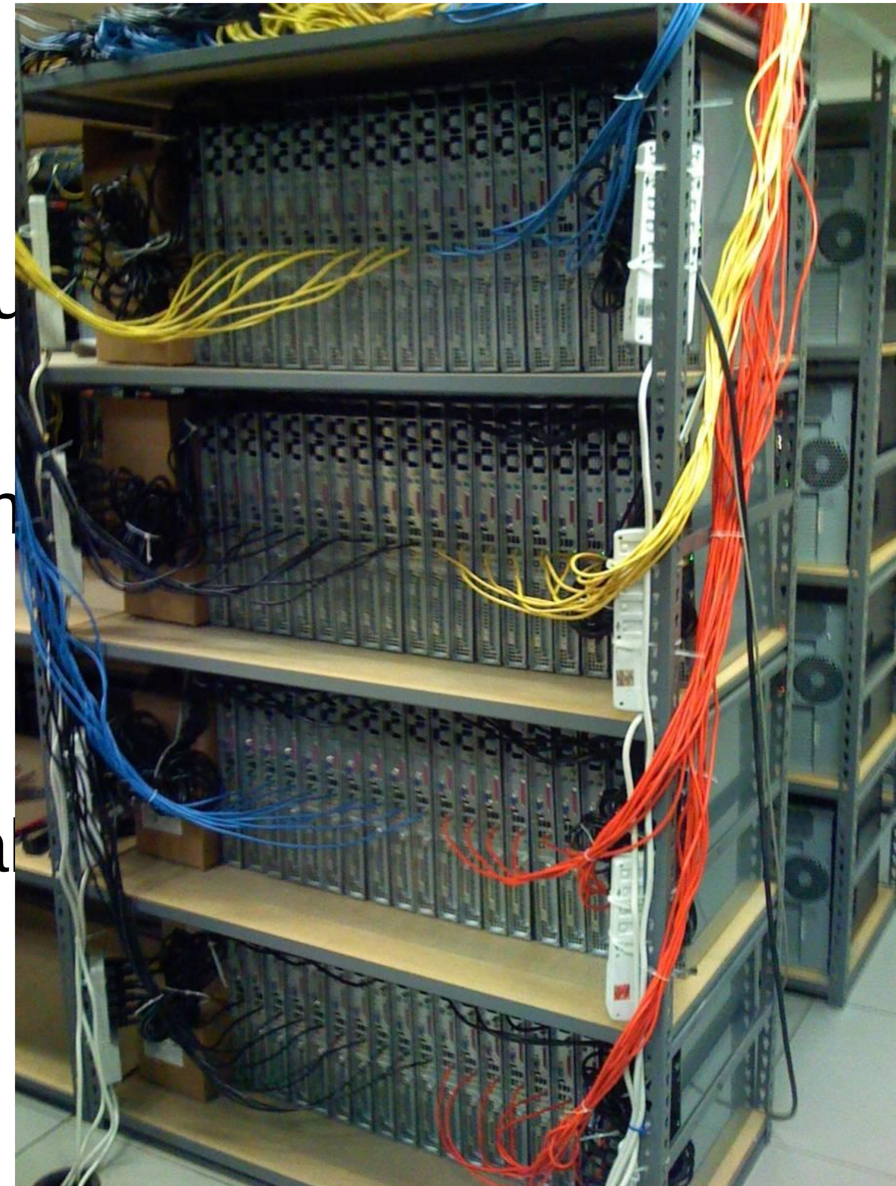
Control Strategy Effectiveness



Source: Kleeman MJ, Ying Q, Kaduwela A. Control strategies for the reduction of airborne particulate nitrate in California's San Joaquin Valley. Atmospheric Environment 39: 5325-5341, 2005.

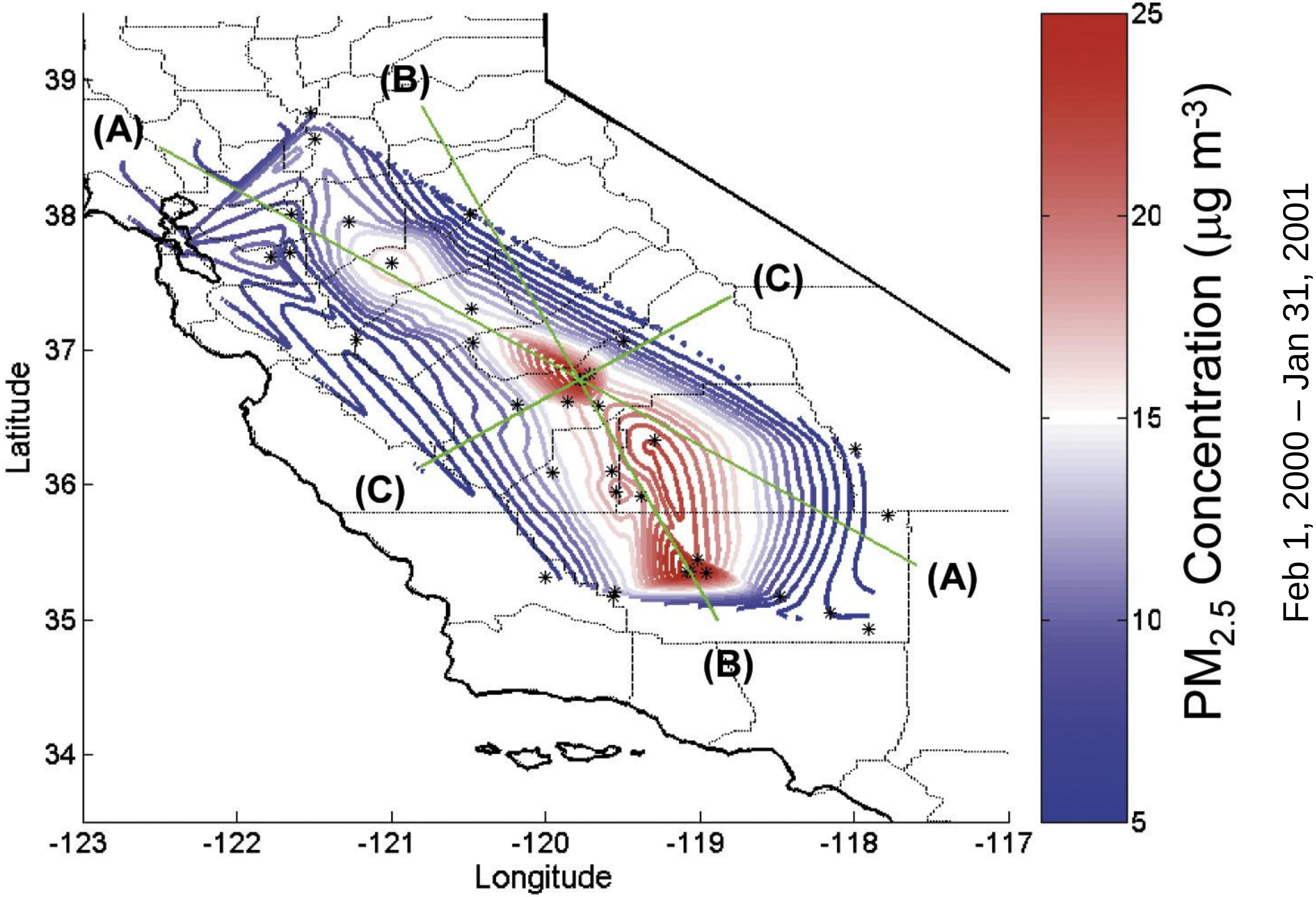
Research vs. Regulatory Models

- Research Model
  - Develop new techniqu
  - Emphasis on science
  - Usually increased con
- Regulatory Model
  - Accepted techniques
  - Emphasis on practical



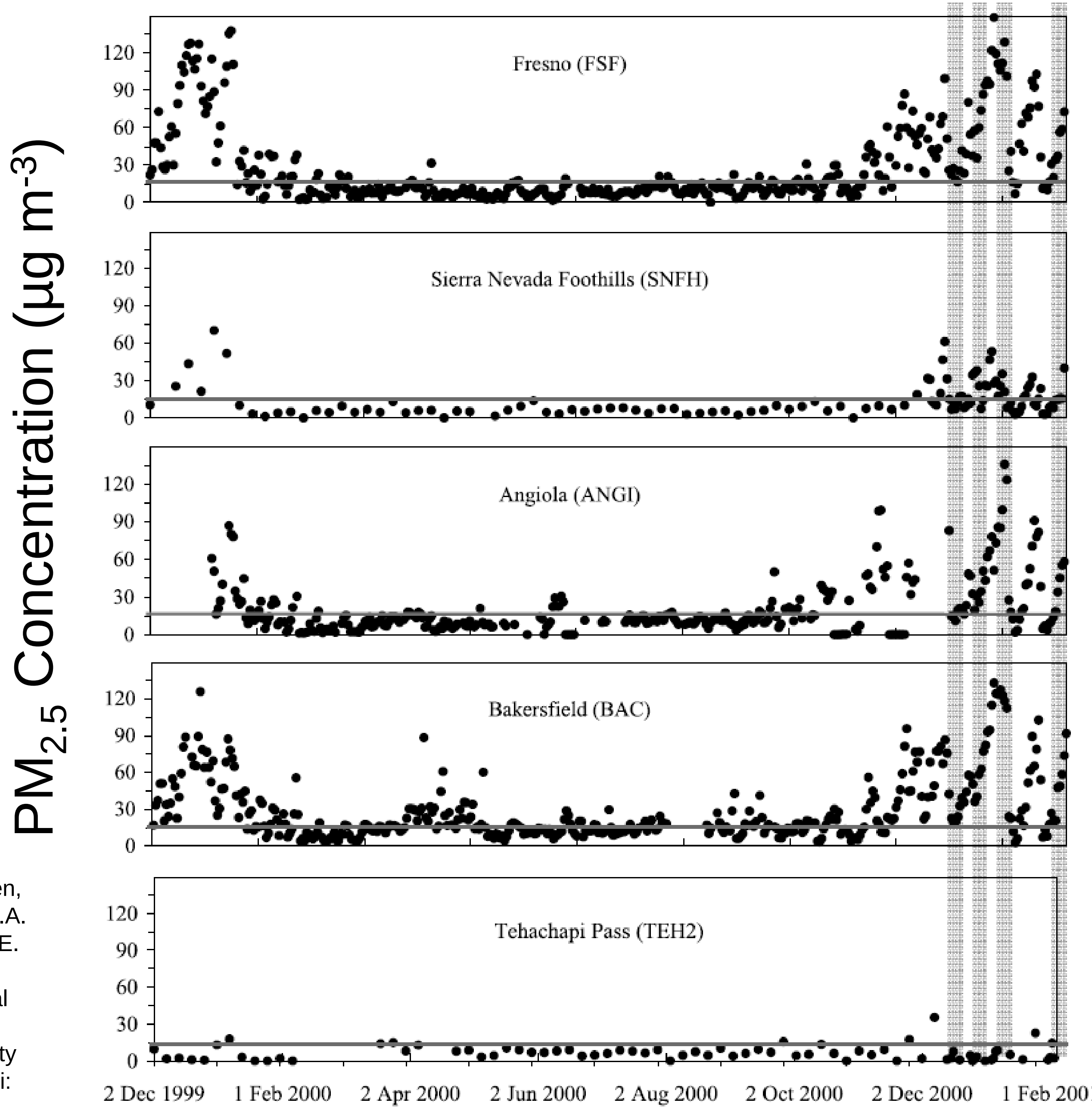
EXTRA SLIDES

PM2.5 Concentrations in the SJV



Source: J.C. Chow, L.W. A. Chen, J.G. Watson, D.H. Lowenthal, K.A. Magliano, K. Turkiewicz, and D.E. Lehrman, "PM2.5 Chemical Composition and Spatiotemporal Variability During the California Regional PM10/PM2.5 Air Quality Study (CRPAQS), JGR, 111, doi: 10.1029/2005JD006457, 2006.

PM2.5 Seasonal Variation in the SJV



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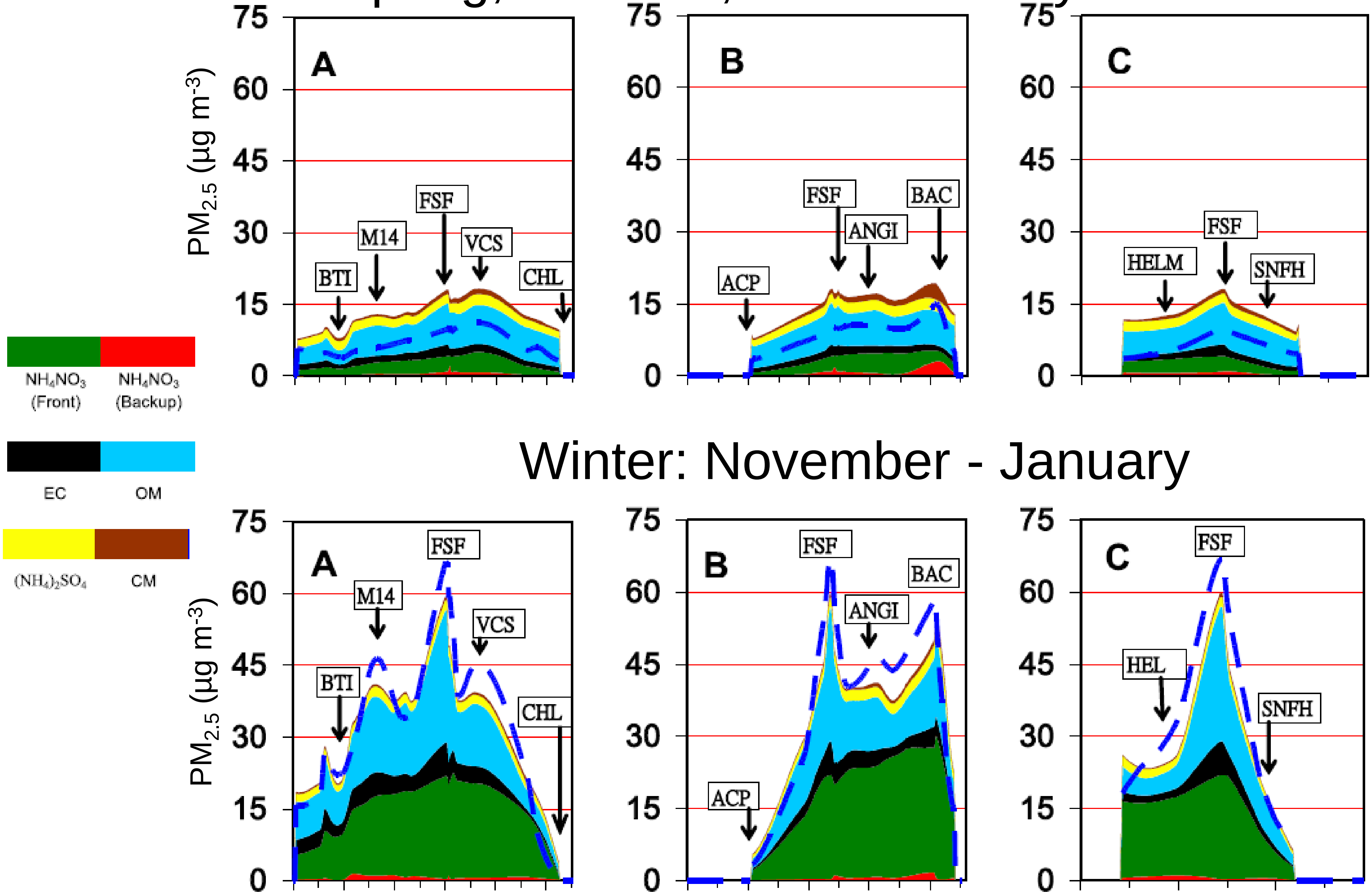
Spring, Summer, Fall: February - October



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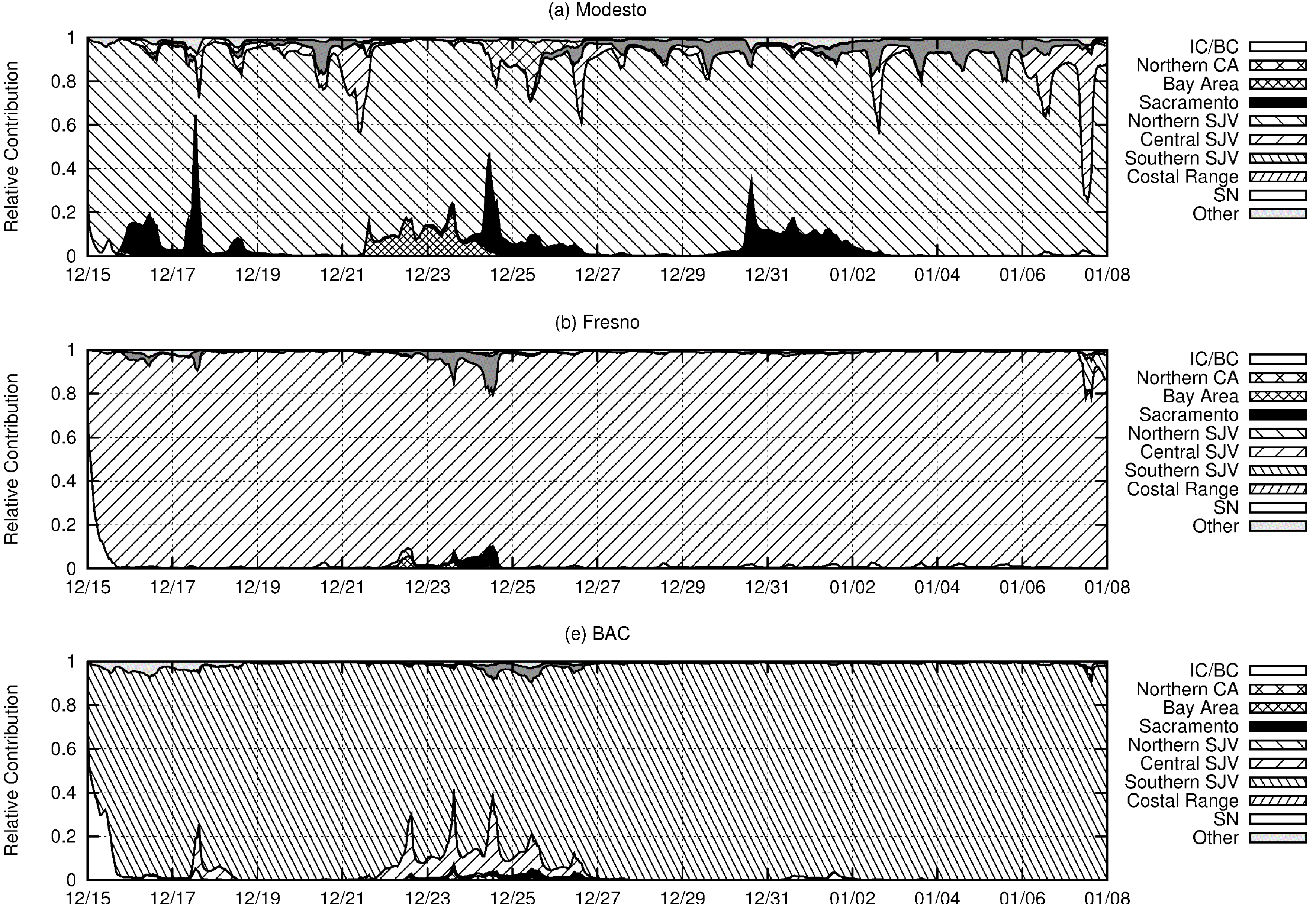
Daytime/Summer Nitrate Formation

- $NO \xrightarrow{O_3} NO_2 \xrightarrow{OH} HNO_3$

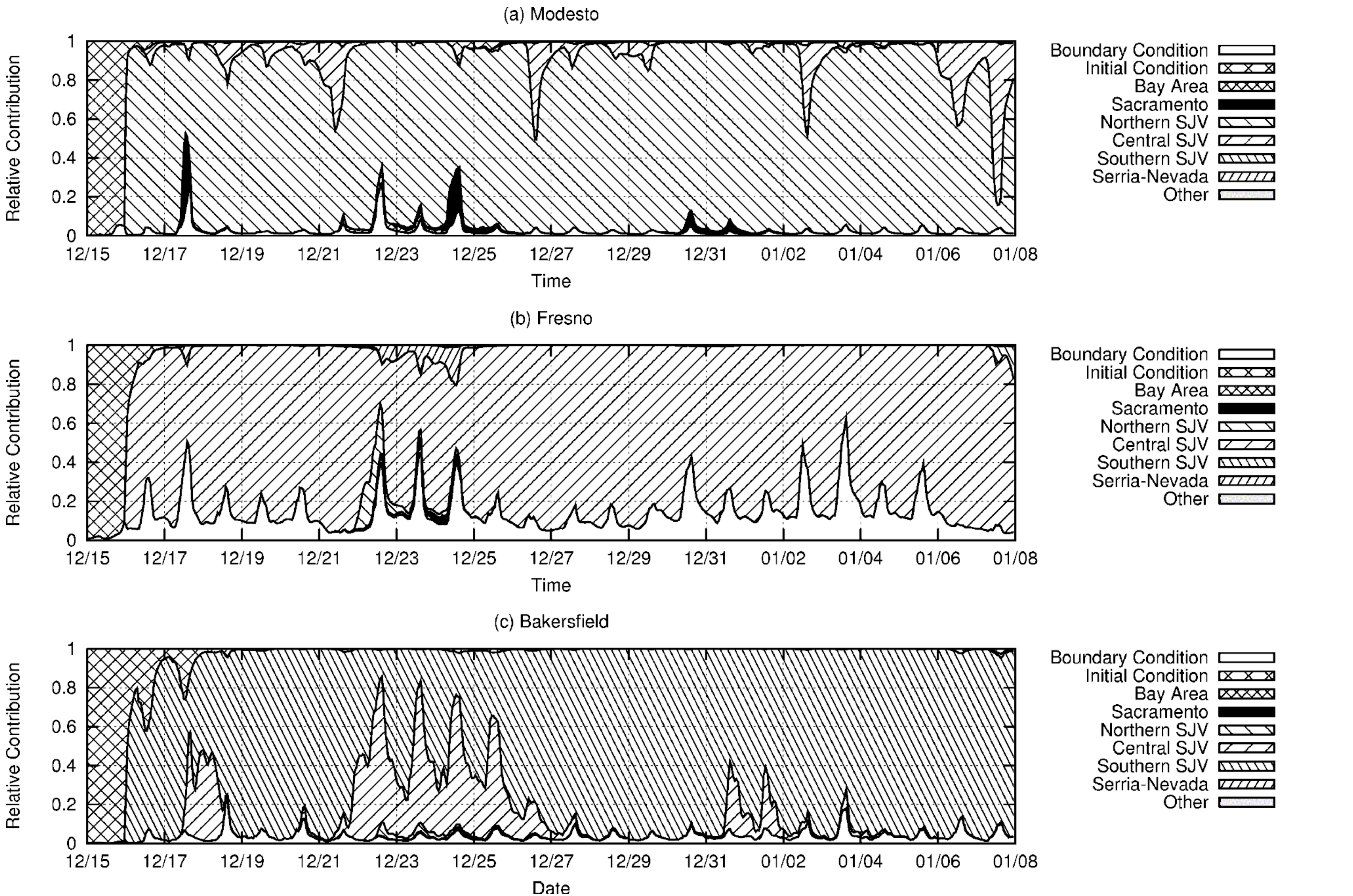
- Main oxidant is OH – requires high sunlight, VOC rich environment

OC Region Contributions



Source: Q. Ying, and M. Kleeman “Regional Contributions to Airborne Particulate Matter in Central California During a Severe Pollution Episode”, Atmos. Env., 43, 1218-1228, 2009.

Ammonium Region Contributions



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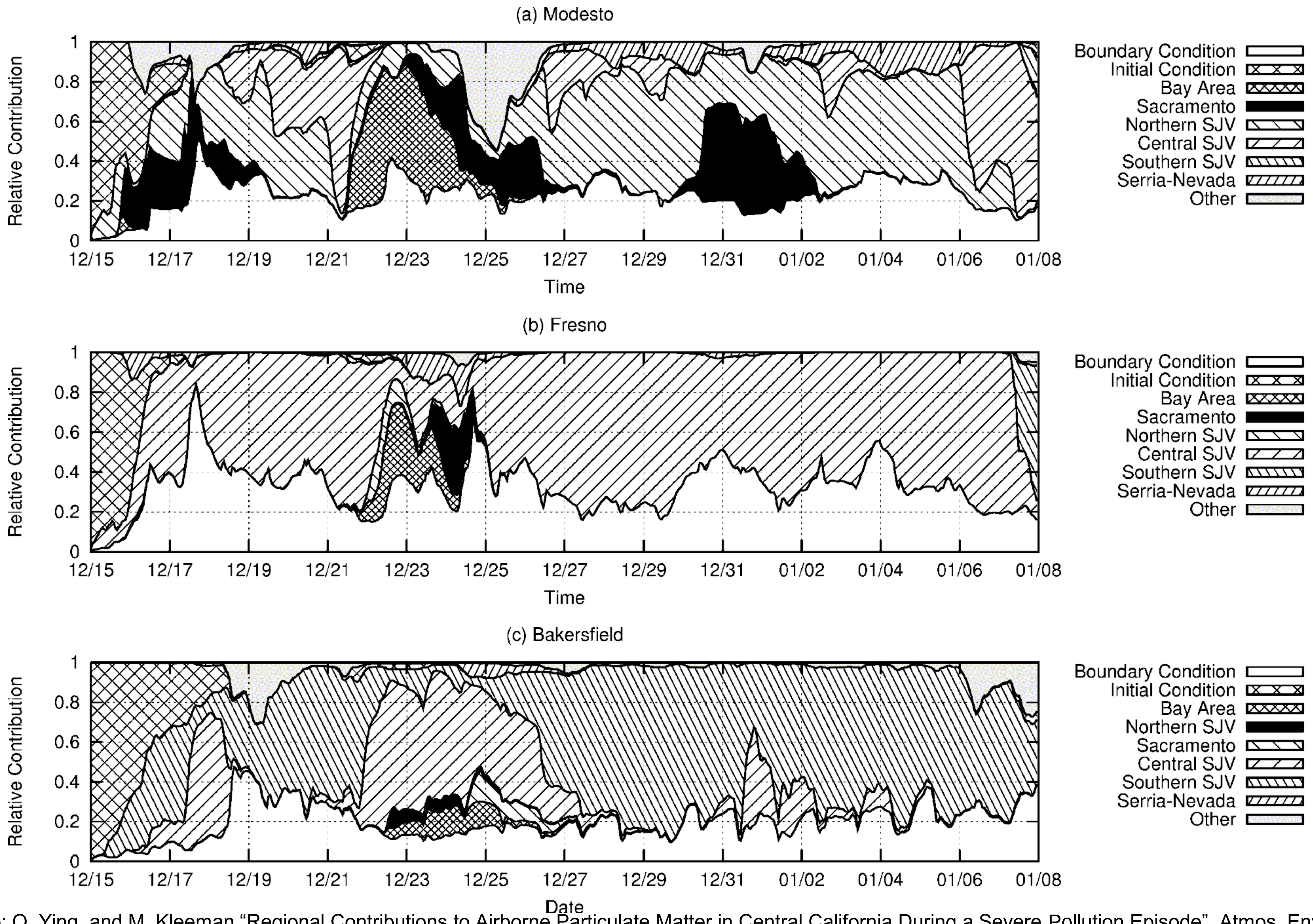
Nitrate Region Contributions



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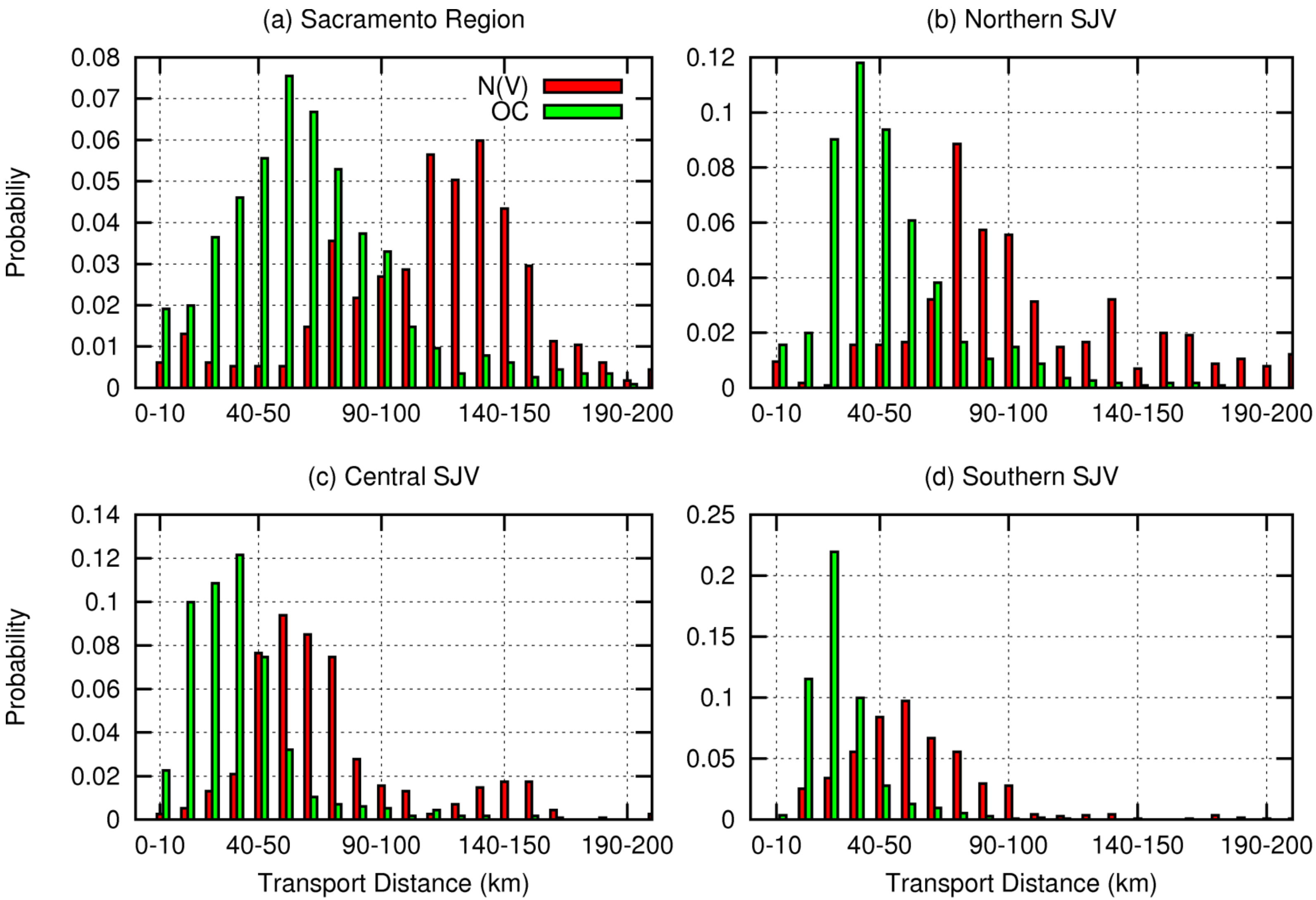
Distribution of Transport Distances



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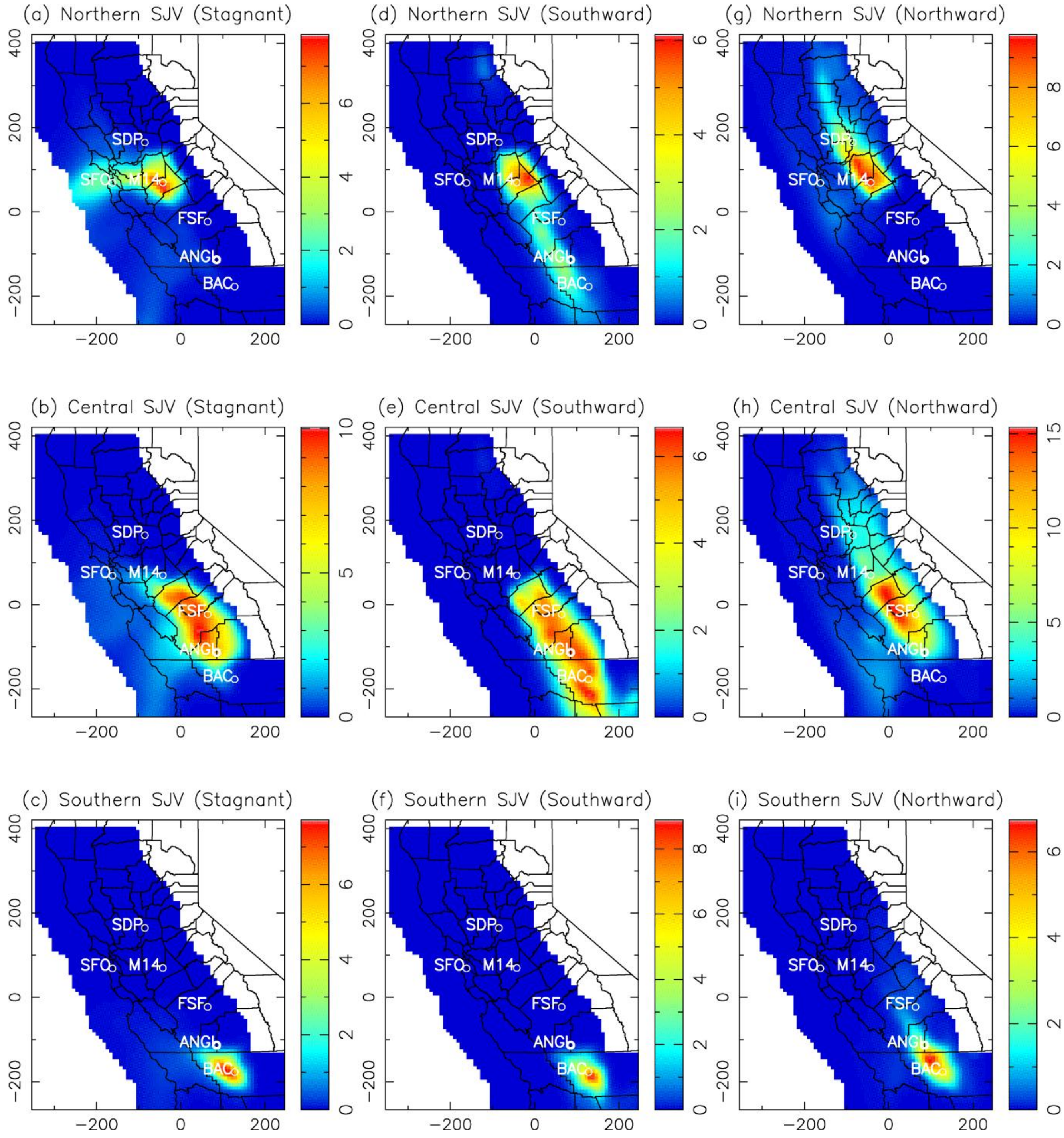
PM2.5 Ammonium



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Nitrate Regional Contribution Summary

Receptor \ Source		BC S0	Bay Area S1	Sac S2	N SJV S3	C SJV S4	S SJV S5	N SacV S6	Sierra S7	Other S8	SUM
Bay Area	R1	2.1%	1.5%	1.8%	1.4%	0.4%	0.0%	0.2%	0.2%	0.7%	8.2%
Sac	R2	1.1%	0.2%	1.3%	0.3%	0.3%	0.0%	0.1%	0.1%	0.8%	4.3%
N SJV	R3	1.3%	0.3%	0.8%	1.7%	1.0%	0.0%	0.1%	0.4%	0.2%	5.9%
C SJV	R4	5.0%	0.8%	0.9%	1.7%	17.7%	0.7%	0.8%	0.4%	0.3%	28.3%
S SJV	R5	1.4%	0.3%	0.2%	0.2%	3.1%	3.1%	0.4%	0.0%	0.2%	9.0%
N SacV	R6	3.4%	1.1%	0.6%	1.1%	4.0%	1.4%	2.0%	0.1%	0.7%	14.5%
Sierra	R7	0.5%	0.1%	0.1%	0.1%	0.3%	0.0%	0.1%	0.2%	0.0%	1.5%
Other	R8	8.4%	3.9%	2.3%	1.7%	2.4%	0.6%	2.3%	0.2%	6.5%	28.4%
	SUM	23.2%	8.2%	8.1%	8.2%	29.3%	6.0%	6.0%	1.6%	9.4%	100.0%

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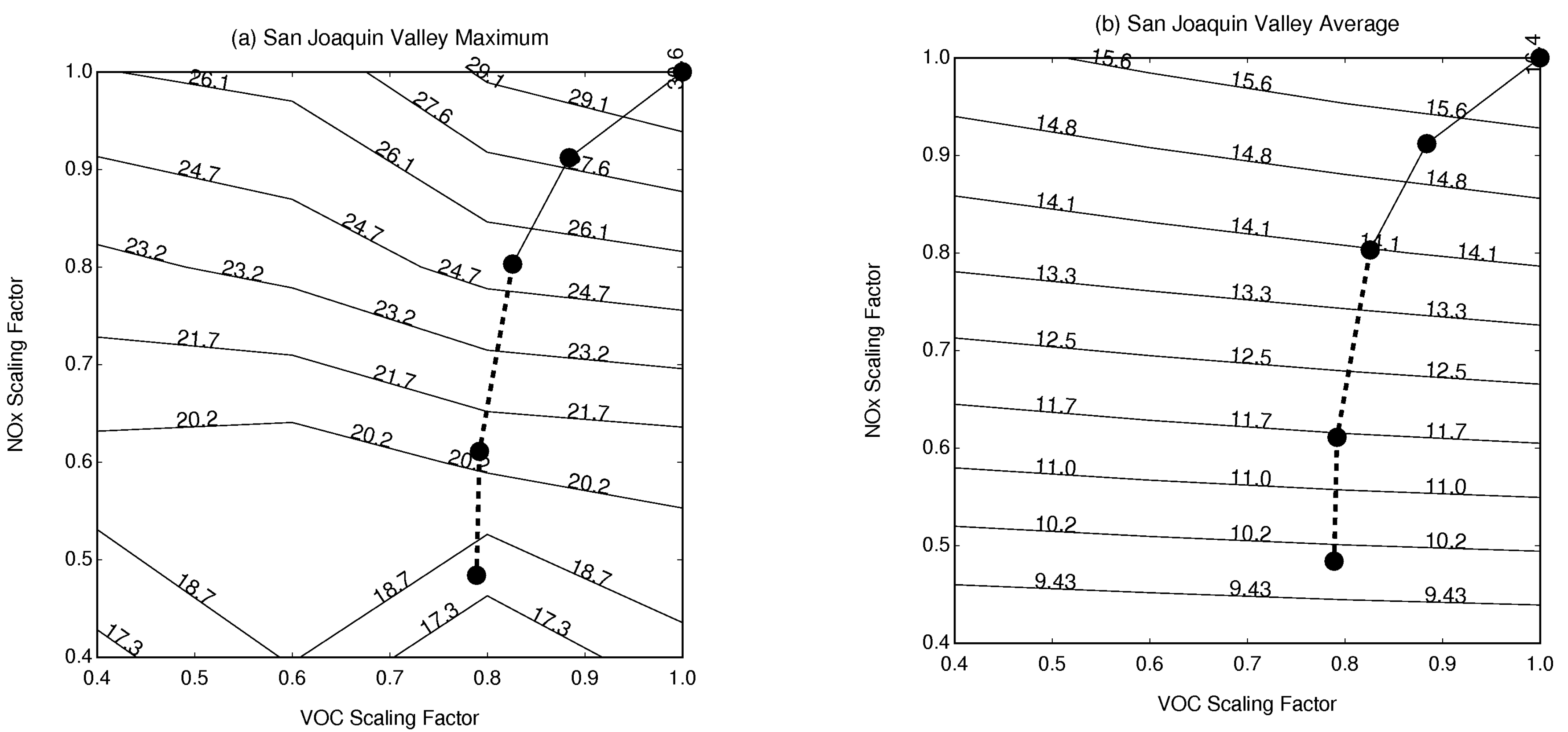
Nitrate Control Options



Maximum 24-hr average PM2.5 nitrate concentrations response to NOx and VOC controls on December 31, 2000 using the SAPRC 90 chemical mechanism. Solid line with dots represents estimated emissions control trajectory since the year 2000 and dashed line with dots represents projected emissions controls through the year 2020 based on the California Almanac for Emissions.

Partial Answers

- *Primary vs. secondary PM 2.5 species*
  - *Elemental carbon (EC), organic carbon (OC), ammonium nitrate*
- *Sources of PM 2.5 in the region?*
  - *Wood smoke (OC) and diesel engines (EC) in urban areas*
  - *Diesel engines (nitrate) and gasoline engines (nitrate) contribute regionally*
  - *Agricultural activities (ammonium) contribute regionally*

Partial Answers

- *Why do they concentrate in winter?*
  - *Lower mixing depths, colder temperature, home heating*
- *Where and when do PM 2.5 concentrations vary in the Valley?*
  - *Transport can be a factor, but mostly local emissions cause local air pollution*
- *What types of control measures have been most successful?*
  - *Restrictions on residential wood combustion*
  - *Restrictions on NO emissions*

Acknowledgements

- Qi Ying, James Chen, Jianlin Hu, Jin Lu
- Karen Magliano, Ajith Kaduwela, Vernon Hughes
- Paul Allen, Paul Livingstone
- Everyone who made measurements during CRPAQS
- Zhan Zhao, Shuhua Chen

- San Joaquin Valleywide Air Pollution Study Agency
- United States Environmental Protection Agency